

TITLE OF THE INVENTION:

Acetylenic Diol Surfactant Solutions and Methods of Using Same

CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** This application is a continuation-in-part of U.S. Patent Application No. 10/218,068, filed 12 August 2002, the disclosure of which is incorporated herein by reference in its entirety.

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BACKGROUND OF THE INVENTION

**[0002]** The present invention relates generally to a method for the manufacture of semiconductor devices. More specifically, the present invention relates to a process solution for treating the surface of a substrate and a method for using same.

10 **[0003]** By the year 2004, the newly updated International Technology Roadmap for Semiconductors (ITRS) states that critical features, as measured by the gate length of MPUs and the  $\frac{1}{2}$  pitch of Dynamic Random Access Memory (DRAM) devices, will break the 100 nm barrier. Critical Dimension (CD) is one process control lever that is closely monitored. At the 90 nm technology node, the CD control, as measured by the 3-sigma  
15 requirement, will approach 3.0 nm which is approximately the size of the polymer molecules that comprise the photoresist. Furthermore, the size of the wafers being processed is growing larger. As a result, this magnitude of control has to be reproduced on larger, 300 mm wafers.

**[0004]** Paralleling the reduction in line geometries is the need for tighter control over  
20 the lithographic process. Lithography is a critical process for the manufacture of semiconductor components and integrated circuits (IC). In brief, the typical lithography

process involves coating a substrate with a positive or negative resist layer, exposing the substrate to a radiation source to provide an image, and developing the substrate to form a patterned resist layer on the substrate. This patterned layer acts as a mask for subsequent substrate patterning processes such as etching, doping, and/or coating with metals, other semiconductor materials, or insulating materials.

**[0005]** One strategy for addressing the need for tighter CD control may be to improve the development process. This approach becomes increasingly important because the next generation of photoresists for 193 nm lithography will be more hydrophobic, and, thus, be more resistant to developer wetting. Poor wetting of the photoresist by the developer can lead to defects as well as a reduction in CD control. It is anticipated that these problems may be amplified with the move towards 300 mm processing because more surface area on the substrate will need to be simultaneously wetted. The current method to improve the wetting on the resist surface prior to photoresist development uses deionized water (DI). This method, however, may not be adequate to prepare the surface of the substrate for the future generation of resists.

**[0006]** The ability to reduce the surface tension of water at the air and liquid interface is of great importance in a variety of applications because decreased surface tension generally relates to increased wetting of water on the substrate surface. Surface tension reduction in water-based systems is generally achieved through the addition of surfactants. Equilibrium surface tension performance is important when the system is at rest, though the ability to reduce surface tension under dynamic conditions is of great importance in applications where high surface creation rates are used, i.e., spin coating, rolling, spray coating, and the like. Dynamic surface tension provides a measure of the ability of the solution to lower surface tension and provide wetting under high speed application conditions. Further, in certain applications such as during spray application,

it is advantageous that the surfactant reduces the surface tension of the formulation in a manner that minimizes bubble generation and foaming.

**[0007]** Surfactants have been added to pre-rinse solutions prior to the development step to improve the contrast in positive photoresist developing. For example, EP

5 0231028 B1 describes treating a photoresist film in a pre-dip bath containing an organic base and cationic solution and rinsing with DI water prior to developing the photoresist film in a developer solution containing an organic base and fluorochemical surfactant. Similarly, EP 0178495 B1 describes treating a photoresist film with a pre-dip solution containing an aqueous alkali metal base and a fluorochemical or carboxylated surfactant and rinsing with DI water prior to developing the photoresist film in a developer solution containing an aqueous alkali metal hydroxide and optionally a fluorochemical or carboxylated surfactant. Both references employ a two-solution process that includes a DI water rinse step between the pre-dip and development steps. It may be desirable, however, to treat the surface of the substrate and achieve the benefits of improved wetting in fewer steps. It may also be desirable to treat the surface of the substrate with a dynamic rather than a static rinse.

**[0008]** Japanese patent application 2002/148821 describes coating a wafer having a fluorine and silicon-based polymer resist with a fluorosurfactant to improve the wettability of the developer.

20 **[0009]** Accordingly, there is a need in the art to provide a process solution to prepare the surface of a substrate prior to development or other steps within the lithography process. There is a further need to provide process solutions that improve the wettability of the surface, for example, by lowering the contact angle of a subsequently applied processing solution on the substrate. There is also a need in the art for process solutions comprising a surfactant that works effectively in high-speed applications

without undesirable foaming or bubble generation. Further, there is a need in the art for a process solution that reduces the number of treatment steps.

**[0010]** All references cited herein are incorporated herein by reference in their entirety.

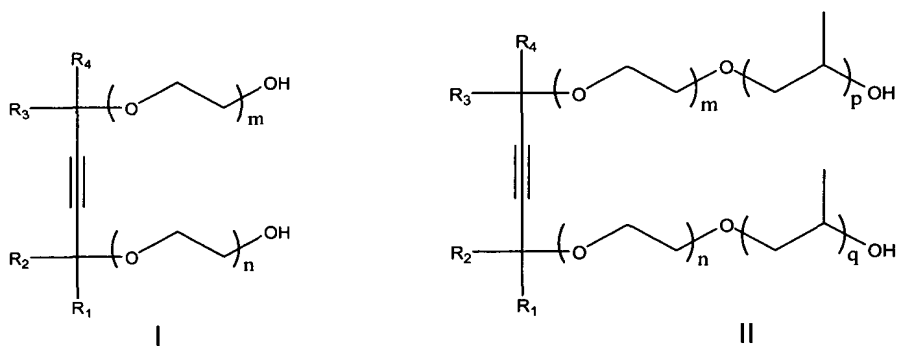
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## BRIEF SUMMARY OF THE INVENTION

**[0011]** The present invention satisfies some, if not all, of the needs of the art by providing a process solution comprising one or more acetylenic diol type surfactants to prepare the surface of a substrate. The process solution of the present invention may be used to modify the character of the substrate surface from a hydrophobic surface to a substantially more hydrophilic surface, or vice versa. As a result of this treatment, the substrate may exhibit improved wettability, enhanced development, improved CD control, reduced defects, and/or increased throughput by achieving faster developing speeds.

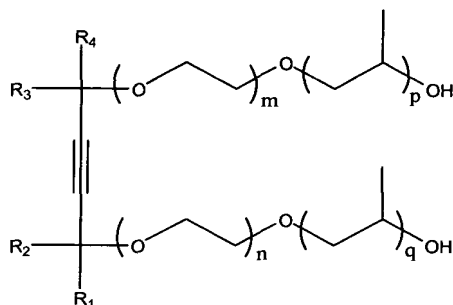
**[0012]** Specifically, in one embodiment of the present invention, there is provided a method for improving the wettability of a substrate. The method comprises the steps of contacting the substrate with a process solution comprising: a solvent selected from the group consisting of an aqueous solvent, a non-aqueous solvent, and combinations thereof; and about 10 ppm to about 10,000 ppm of at least one surfactant having the formula (I) or (II):

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wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and m, n, p, and q are numbers that range from 0 to 20; coating the substrate with a resist coating to provide a resist-coated substrate; exposing at least a portion of the resist-coated substrate to a radiation source for a time sufficient to provide a pattern on the resist coating; and applying the aqueous developer solution to the substrate to dissolve at least a portion of the resist coating. In certain embodiments, the contacting step may be performed prior to the applying step.

**[0013]** In a further embodiment of the present invention, there is provided a method for improving the wettability of a substrate. The method comprises the steps of contacting a substrate with a process solution comprising: a solvent selected from the group consisting of an aqueous solvent, a non-aqueous solvent, and combinations thereof; and about 10 ppm to about 10,000 ppm of at least one surfactant having the formula:

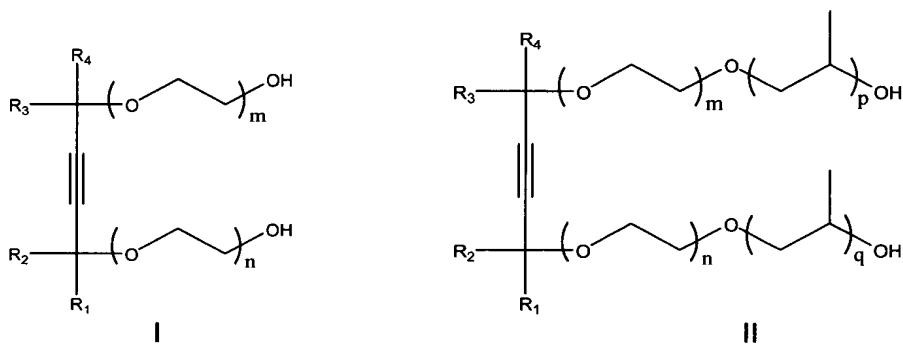


wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and m, n, p, and q are numbers that range from 0 to 20; coating the substrate with a resist coating to provide a resist-coated substrate; exposing at least a portion of the resist-coated substrate to a radiation source for a time sufficient to provide a pattern on the resist coating; and applying the aqueous developer solution to the substrate to dissolve

at least a portion of the resist coating. In certain embodiments, the contacting step is performed prior to the applying step.

**[0014]** In yet another embodiment of the present invention, there is provided a method for improving the wettability of a substrate by lowering the contact angle of an aqueous developer solution on the surface of the substrate. The method comprises the steps of

5 contacting the substrate with a process solution comprising: a solvent selected from the group consisting of an aqueous solvent, a non-aqueous solvent, and combinations thereof; and about 10 ppm to about 10,000 ppm of at least one surfactant having the formula (I) or (II):



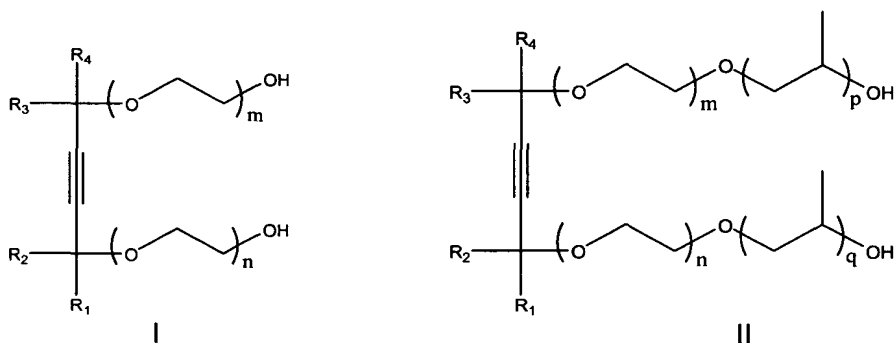
wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and m,

15 n, p, and q are numbers that range from 0 to 20; coating the substrate with a resist coating to provide a resist-coated substrate; exposing at least a portion of the resist-coated substrate to a radiation source for a time sufficient to provide a pattern on the resist coating; contacting the resist-coated substrate with the process solution; and

20 applying an aqueous developer solution to the substrate to dissolve at least a portion of the resist coating.

**[0015]** In yet another embodiment of the present invention, there is provided a process solution comprising: a solvent selected from the group consisting of an aqueous solvent,

a non-aqueous solvent, and combinations thereof and about 10 to about 10,000 ppm of at least one surfactant having the formula (I) or (II):

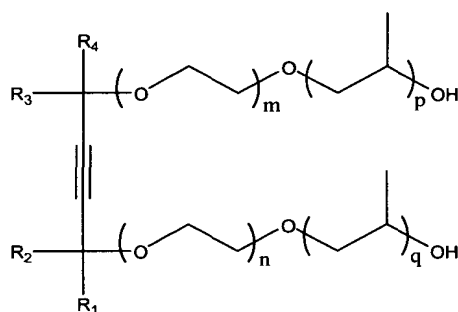


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wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and  $m$ ,  $n$ ,  $p$ , and  $q$  are numbers that range from 0 to 20.

**[0016]** In a still further embodiment of the present invention, there is provided a process solution comprising: a solvent selected from the group consisting of an aqueous solvent, a non-aqueous solvent, and combinations thereof; and about 10 to about 10,000 ppm of a surfactant having the formula:

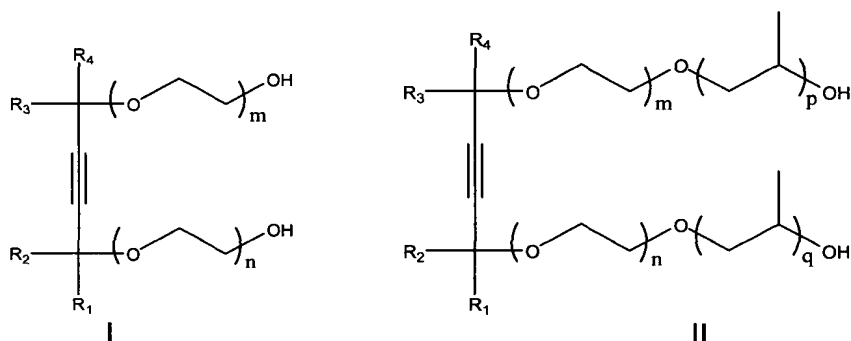
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wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and  $m$ ,  $n$ ,  $p$ , and  $q$  are numbers that range from 0 to 20.

**[0017]** In a yet another aspect of the present invention, there is provided a method for improving the wettability of an aqueous developer solution on a surface of a resist-coated substrate comprising: providing a process solution comprising: a solvent selected from the group consisting of an aqueous solvent, a non-aqueous solvent, and combinations thereof; and about 10 ppm to about 10,000 ppm of at least one surfactant having the formula (I) or (II):



wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and  $m$ ,  $n$ ,  $p$ , and  $q$  are numbers that range from 0 to 20; contacting the resist-coated substrate with the aqueous solution; and applying the aqueous developer solution to the resist-coated substrate wherein the contacting step is conducted prior to the applying step.

**[0018]** These and other aspects of the invention will become apparent from the following detailed description.

## DETAILED DESCRIPTION OF THE INVENTION

**[0019]** The present invention is directed to process solutions having at least one surfactant that is an acetylenic diol derivative and methods for using same. The process solution of the present invention may be used to modify the character of the substrate surface from a hydrophobic surface to a substantially more hydrophilic surface, or vice versa. For example, in certain embodiments, the process solution of the present



invention may be used to treat a surface of a substrate that be coated with a layer of resist coating prior to the development of the resist. In this manner, the wettability of the substrate surface may be improved.

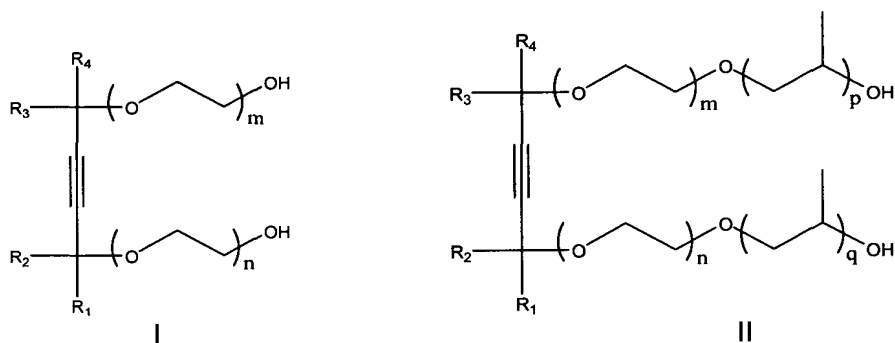
**[0020]** The term “aqueous” as used herein, describes a solvent or liquid dispersing medium, which comprises at least 80 weight percent, preferably 90 weight percent, and more preferably at least 95 weight percent water. The preferred aqueous-based solvent is deionized water. In embodiments wherein the process solution is aqueous-based, it is desirable that at least one formula I through VIII surfactant demonstrates a dynamic surface tension of less than 45 dynes/cm at a concentration of less than or equal to 5 weight percent in water at 23°C and 1 bubble/second according to the maximum-bubble-pressure method of measuring surface tension described in *Langmuir* 1986, 2, 428-432, which is incorporated herein by reference in its entirety.

**[0021]** In embodiments where a non-aqueous solvent is used in addition to, or in place of an aqueous solvent such as water, the non-aqueous solvent selected will not react with the at least one surfactant contained therein, other additives within the process solution, or the substrate itself. Suitable solvents include, but are not limited to, hydrocarbons (e. g. pentane or hexane); halocarbons (e. g. Freon 113); ethers (e. g. ethylether (Et<sub>2</sub>O), tetrahydrofuran (“THF”), ethylene glycol monomethyl ether, or 2-methoxyethyl ether (diglyme)); nitriles (e. g. CH<sub>3</sub>CN); or aromatic compounds (e.g. benzotrifluoride). Still further exemplary solvents include lactates, lactones, pyruvates, and diols. These solvents include, but are not limited to, acetone, 1,4-dioxane, 1,3-dioxolane, ethyl acetate, cyclohexanone, acetone, 1-methyl-2-pyrrolidone (NMP),  $\gamma$ -butyrolactone, methyl ethyl ketone. Other solvents include dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, ethylene carbonate, propylene carbonate, glycerol and derivatives, naphthalene and substituted versions, acetic acid anhydride, propionic acid and propionic acid anhydride, dimethyl sulfone, benzophenone, diphenyl

sulfone, phenol, m-cresol, dimethyl sulfoxide, diphenyl ether, terphenyl, and the like. Still further solvents include propylene glycol propyl ether (PGPE), methanol, ethanol, 3-heptanol, 2-methyl-1-pentanol, 5-methyl-2-hexanol, 3-hexanol, 2-heptano, 2-hexanol, 2,3-dimethyl-3-pentanol, propylene glycol methyl ether acetate (PGMEA), ethylene glycol, isopropyl alcohol (IPA), n-butyl ether, propylene glycol n-butyl ether (PGBE), 1-butoxy-2-propanol, 2-methyl-3-pentanol, 2-methoxyethyl acetate, 2-butoxyethanol, 2-ethoxyethyl acetoacetate, 1-pentanol, and propylene glycol methyl ether. The non-aqueous solvents enumerated above may be used alone or in combination with one or more aqueous or non-aqueous solvents.

10 **[0022]** In certain embodiments, the process solution may contain at least one non-aqueous solvent that is miscible in an aqueous solvent or is water-miscible. In these embodiments, the amount of non-aqueous solvent within the process solution may range from about 1 to about 50 % by weight with the balance of the solvent within the process solution comprising an aqueous solvent. Examples of water-miscible non-aqueous solvents include methanol, ethanol, isopropyl alcohol, and THF.

15 **[0023]** The process solutions of the present invention contain one or more nonionic surfactants that are acetylenic diol derivatives. The surfactants of the present invention may be represented by the following formula I or formula II:



wherein  $R_1$  and  $R_4$  are a straight or a branched alkyl chain having from 3 to 10 carbon atoms;  $R_2$  and  $R_3$  are either H or an alkyl chain having from 1 to 5 carbon atoms; and  $m$ ,  $n$ ,  $p$ , and  $q$  are numbers that range from 0 to 20. The surfactants are commercially available from Air Products and Chemicals, Inc. of Allentown, PA, the assignee of the present invention, under the trade names SURFYNOL® and DYNOL®. In certain preferred embodiments, the acetylenic diol portion of the molecule of formulas I or II is 2,4,5,9-tetramethyl-5-decyne-4,7-diol or 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol. The acetylenic diol derived surfactants of the present invention may be prepared in a number of ways including the methods described, for example, in U. S. Pat. No. 6,313,182 and EP 1115035A1 which are assigned to the assignee of the present invention and incorporated herein by reference in their entirety.

**[0024]** In formula I and II, the alkylene oxide moieties represented by  $(OC_2H_4)$  are the  $(n + m)$  polymerized ethylene oxide (EO) molar units and the moieties represented by  $(OC_3H_6)$  are the  $(p + q)$  polymerized propylene oxide (PO) molar units. The value of  $(n + m)$  may range from 0 to 30, preferably from 1.3 to 15, and more preferably from 1.3 to 10. The value of  $(p + q)$  may range from 0 to 30, preferably from 1 to 10, and more preferably from 1 to 2.

**[0025]** In certain embodiments, the process solution may contain a dispersant. The amount of dispersant that is added to the process solution ranges from about 10 to about 10,000 ppm, preferably about 10 to about 5,000 ppm, and more preferably from about 10 to about 1,000 ppm. The term dispersant, as used herein, describes compounds that enhance the dispersion of particles such as dust, processing residue, hydrocarbons, metal oxides, pigment or other contaminants within the process solution. Dispersants suitable for the present invention preferably have a number average molecular weight that ranges from about 10 to about 10,000.

**[0026]** In certain preferred embodiments, the dispersant may be an ionic or a nonionic compound. The ionic or nonionic compound may further comprise a copolymer, an oligomer, or a surfactant, alone or in combination. The term copolymer, as used herein, relates to a polymer compound consisting of more than one polymeric compound such as block, star, or grafted copolymers. Examples of a nonionic copolymer dispersant include polymeric compounds such as the tri-block EO-PO-EO co-polymers PLURONIC® L121, L123, L31, L81, L101 and P123 (BASF, Inc.). The term oligomer, as used herein, relates to a polymer compound consisting of only a few monomer units. Examples of ionic oligomer dispersants include SMA® 1440 and 2625 oligomers (Elf Alfochem).

**[0027]** The dispersant may further comprise a surfactant. Typical surfactants exhibit an amphiphilic nature, meaning that they can be both hydrophilic and hydrophobic at the same time. Amphiphilic surfactants possess a hydrophilic head group or groups, which have a strong affinity for water and a long hydrophobic tail, which is organophilic and repels water. The surfactants may be ionic (i.e., anionic, cationic) or nonionic. Further examples of surfactants include silicone surfactants, poly(alkylene oxide) surfactants, and fluorochemical surfactants. Suitable non-ionic surfactants for use in the process solution include, but are not limited to, octyl and nonyl phenol ethoxylates such as TRITON® X-114, X-102, X-45, X-15 and alcohol ethoxylates such as BRIJ® 56 (C<sub>16</sub>H<sub>33</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>10</sub>OH) (ICI), BRIJ® 58 (C<sub>16</sub>H<sub>33</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>20</sub>OH) (ICI). Still further exemplary surfactants include alcohol (primary and secondary) ethoxylates, amine ethoxylates, glucosides, glucamides, polyethylene glycols, poly(ethylene glycol-co-propylene glycol), or other surfactants provided in the reference *McCutcheon's Emulsifiers and Detergents*, North American Edition for the Year 2000 published by Manufacturers Confectioners Publishing Co. of Glen Rock, N.J.

**[0028]** Various other additives may be optionally added to the process solution depending upon the application. These additives may include, but are not limited to, colorants, wetting agents, antifoamers, buffering agents, and other surfactants.

Generally, the amount of each of these additives would be about 0.0001 to 1, more preferably 0.0001 to 0.1 percent by weight, based upon the total weight of the process solution. In embodiments where one or more additional surfactant is added to the process solution, the surfactant may be any of the surfactants disclosed herein.

**[0029]** The process solution of the present invention may be prepared by mixing the acetylenic diol derivative surfactant with water and/or other solvents and any additional additives. In certain embodiments, the mixing may be done at a temperature range of about 40 to 60°C to affect dissolution of the ingredients contained therein. The resulting process solution may optionally be filtered to remove any undissolved particles that could potentially harm the substrate.

**[0030]** The process solution of the present invention is applied to, or contacts, the surface of a substrate. Suitable substrates include, but are not limited to, materials such as gallium arsenide ("GaAs"), silicon, tantalum, copper, ceramics, aluminum/copper alloys, polyimides, and compositions containing silicon such as crystalline silicon, polysilicon, amorphous silicon, epitaxial silicon, silicon dioxide ("SiO<sub>2</sub>"), silicon nitride, doped silicon dioxide, and the like. Further exemplary substrates include silicon, aluminum, or polymeric resins. In certain embodiments, the surface of the substrate may be primed with a conventional adhesion promoter such as hexamethyldisilazane (HMDS) before a resist coating is applied. In certain preferred embodiments of the present invention, however, the treatment of the surface with the process solution of the present invention prior to resist coating eliminates the need for HMDS.

**[0031]** The process solution may be used to treat the surface of a substrate before and/or after the surface of the substrate has been coated with a resist coating. In other

words, the contacting step may occur in one or more steps either before and/or after the substrate has been coated with resist. In embodiments wherein the contacting step occurs before coating the substrate with resist, the process solution may improve the wetting of the resist coating to the substrate surface. In this case, the process solution  
5 alters the character of the surface from a more hydrophilic nature to a more hydrophobic one, facilitating the subsequent coating of a hydrophobic organic material such as resist or low-k dielectrics. In embodiments wherein the contacting step occurs after coating the substrate with resist, the process solution may improve the wetting of the aqueous developer solution to the resist-coated surface. In this case, it is believed that the  
10 application of the process solution may alter the character of the surface from a more hydrophobic surface to a more hydrophilic surface.

**[0032]** In certain preferred embodiments, the contacting step occurs after the substrate has been coated with a resist coating. Some non-limiting examples of resist coatings include phenolic resists; resist coatings for 157 nm line widths; resist coatings for 193 nm  
15 line widths such as IBM COBRA 3000 (cyclic olefine) and JSR AT 5000 (COMA) having iodonium photo acid generators (PAGs); deep ultraviolet (DUV) resists such as Shipley ApexE (modified polyhydroxystyrene) and Shipley UV6 (copolymer of hydroxystyrene and t-butyl acrylate); and e-beam resist material such as poly(methylmethacrylate) (PMMA). In certain embodiments of the present invention, the substrate may be also  
20 coated with an antireflective coating (ARC). Examples of suitable ARC coatings used may be any of the coatings manufactured by Brewer Science and Shipley Co. of Marlborough, Mass.

**[0033]** After the resist-coating is applied, the substrate may be baked to evaporate any solvent in the resist composition and to harden the coating onto the substrate. The  
25 resist-coated substrate is then exposed to a radiation source to provide a design pattern that is imposed upon the exposed areas of the resist-coated surface. Examples of

suitable radiation sources include, but are not limited to, visible light, ultraviolet (UV) light, deep ultraviolet (DUV) light, 157 nm, extended ultraviolet (UV) light, electron beam, or X-ray radiant energy.

**[0034]** Depending upon whether the resist coating is positive or negative, the radiation  
5 either increases or decreases its solubility in a subsequently applied, alkaline aqueous developer such as a solution containing tetramethylammonium hydroxide (TMAH). In a positive resist coating, the areas masked from radiation remain after development while the exposed areas are dissolved away. In a negative resist coating, the opposite occurs. In certain preferred embodiments of the present invention, the process solution may be  
10 used to treat substrates having a positive resist coating.

**[0035]** The process solution is preferably applied to the surface of the substrate as a prepared solution. In alternative embodiments, however, the process solution can be prepared within the rinse stream just prior to or during contact with the substrate surface. For example, a certain quantity of one or more acetylenic diol derived surfactants can be  
15 injected into a continuous stream of water or other solvent medium that optionally includes other additives thereby forming the process solution. In some embodiments of the present invention, the at least one surfactant can be also deposited upon or comprise the material of a high surface area device such as a cartridge or filter (which may or may not include other additives). A stream of water and/or solvent then passes through the  
20 cartridge or filter thereby forming the process solution. In still another embodiment of the present invention, the process solution is prepared during the contacting step. In this connection, at least one surfactant is introduced via a dropper or other means to the surface of the substrate. Water and/or other solvent medium is then introduced to the surface of the substrate and mixes with the at least one surfactant on the surface of the  
25 substrate thereby forming the process solution.

**[0036]** In an alternative embodiment of the invention, a concentrated composition is provided that may be diluted in water and/or other solvents to provide the process solution. A concentrated composition of the invention, or "concentrate" allows one to dilute the concentrate to the desired strength and pH. A concentrate also permits longer shelf life and easier shipping and storage of the product.

**[0037]** A variety of means can be employed in contacting the process solution with the substrate surface. The actual conditions of the contacting step (i.e., temperature, time, and the like) may vary over wide ranges and are generally dependent on a variety of factors such as, but not limited to, the nature and amount of residue on the surface of the substrate and the hydrophobicity or hydrophilicity of the substrate surface, etc. The contact step can be conducted in either a dynamic method such as, for example, a streamline process for applying the process solution over the surface of the substrate or in a static method such as, for example, a puddle rinse or immersing the substrate within a bath containing the process solution. The process solution may also be sprayed onto the surface of the substrate in a dynamic method such as in a continuous process or sprayed onto the surface and allowed to remain there in a static method. In certain preferred embodiments, the contacting step is conducted in a dynamic method. The duration of the conducting step, or time of contact of the process solution to the substrate surface, can vary from a fraction of a second to hundreds of seconds. Preferably, the duration can range from 1 to 200 seconds, preferably from 1 to 150 seconds, and more preferably from 1 to 40 seconds. The temperature range for the contacting step can vary from 10 to 100°C and more preferably from 10 to 40°C.

**[0038]** In certain embodiments of the present invention, the substrate may be dried to remove any residual water (and any solvent if added) used to deliver the acetylenic diol type surfactant to the substrate surface. The residual water may be substantially removed via spinning, heating, air drying or other means, to leave a thin film of



acetylenic diol surfactant(s) on the the substrate surface. For example, the substrate may be spun at a speed of 500 rpm to drive off the majority of water in the process solution. The drying step may occur after each application of the process solution, i.e., prior to coating the substrate with resist and/or prior to applying the aqueous developer solution.

**[0039]** The wettability of a subsequently applied aqueous-based solution, such as an alkaline aqueous developer solution, can be determined, for example, by measuring the contact angle. In certain preferred embodiments of the present invention, the contact angle of the aqueous developer solution on the surface of a resist-coated substrate is measured at a time interval of 30 seconds.

**[0040]** The invention will be illustrated in more detail with reference to the following examples, but it should be understood that the present invention is not deemed to be limited thereto. In this connection, the process solution of the present invention, and methods for using same, may be used in other applications in which a substrate surface needs to be treated to enhance wettability of a subsequently applied fluid. For the following examples, the wettability of the process solution was measured on the DSA10 Kruss drop shape analyzer provided by Kruss USA of Charlotte, N.C. using the Sessile drop method. In this method, the wetting properties of a localized region on the surface of a resist-coated substrate are estimated by measuring the contact angle between the baseline of a droplet of aqueous developer solution and the tangent at the droplet base. A high-speed camera captured the spreading of the droplet at a speed of 2 frames per second for 2 minutes and the contact angle was measured.

## EXAMPLES

### Comparative Example 1: Pre-Treatment of A Resist-Coated Substrate Surface with Deionized Water (DI)

**[0041]** A 100 mm silicon wafer provided by Wafernet Inc. of San Jose, Ca. was coated with a SFR 510A phenolic resist coating provided by Shipley Inc. of Marlborough, Mass. using a spin coating process at a spin speed of 3200 rpm. Deionized water is dispensed via dropper onto the surface of the resist-coated wafer that is spinning at a speed of 200 rpm. The resist-coated wafer was allowed to dry for a period of 20 seconds to remove excess water. Afterwards, the contact angle of 0.26N TMAH developer on the resist-coated surface was measured. Table I provides the value of the contact angle at different drop ages expressed in seconds.

### Examples 1a through 1d: Pre-Treatment of A Resist-Coated Substrate Surface with Process Solutions of the Present Invention

**[0042]** Process solutions of surfactant based on 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol ( $m + n = 4$ ,  $p + q = 0$ ), surfactant provided by Air Products and Chemicals, Inc. of Allentown, PA, were prepared in the following manner. A volumetric flask was charged with varying amounts of the surfactant. A certain amount of DI water was added to the volumetric flask to reach a level of 100 ml at room temperature. The mixture was agitated until the surfactant was dissolved therein to form the process solution. The amounts of surfactant in the process solutions of Examples 1a through 1d are provided in Table I.

**[0043]** Four 100 mm silicon wafers provided by Wafernet Inc. of San Jose, Ca. were coated with a SFR 510A phenolic resist coating provided by Shipley Inc. of Marlborough, Mass. using a spin coating process at a spin speed of 3200 rpm. The surfaces of resist-coated substrates were pre-wetted with Examples 1a through 1d process solutions. The

resist-coated wafer was allowed to dry for a period of 20 seconds to remove excess water. Afterwards, the contact angle of 0.26N TMAH on the resist-coated substrates was measured. Table I lists the contact angle values at different drop ages expressed in seconds.

- 5 **[0044]** As Table I illustrates, the contact angles of TMAH developer on the resist-coated substrate that were treated with the process solutions of the present invention are smaller than the ones for the resist-coated substrates treated with DI water only. This indicates that surfactants are better adsorbed onto resist-coated surfaces that are treated with the process solutions of the present invention thereby improving the wetting
- 10 between the developer and resist. Further, higher amounts of surfactant within the process solution may lead to more surfactant adsorption and more improved wetting.

TABLE I

Process Solution	Contact Angle (0 seconds)	Contact Angle (5 seconds)	Contact Angle (10 seconds)	Contact Angle (30 seconds)
Comp. Ex. 1 – DI water	51.7	49.7	48.6	45.8
Ex. 1a - 60 ppm surfactant	60.5	50.4	46.6	39.4
Ex. 1b –125ppm surfactant	59.4	45.7	41.4	33.7
Ex. 1c -250ppm surfactant	49.0	40.3	37.0	31.1
Ex. 1d -400 ppm surfactant	47.3	37.4	34.5	29.1

- Comparative Example 2: Pre-Treatment of A Resist-Coated Substrate Surface with DI
- 15 Water

**[0045]** A 100 mm silicon wafer provided by Wafernet of San Jose, Ca. was coated with a SFR 510A phenolic resist coating provided by Shipley Inc. of Marlborough, Mass. using a spin coating process at a spin speed of 3200 rpm. Deionized water is dispensed

via dropper onto the wafer coated wafer that is spinning at a speed of 200 rpm. The resist-coated surface was allowed to dry for a period of 20 seconds to remove excess water. Afterwards, the contact angle of 0.26N TMAH developer on the resist surface was measured. Table II provides the value of the contact angle at different drop ages expressed in seconds.

#### Examples 2a through 2d: Pre-Treatment of A Resist-Coated Substrate Surface with Process Solutions of the Present Invention

**[0046]** Process solutions of surfactant based on 2,4,7,9-tetramethyl-5-decyne-4,7-diol ( $m + n=5$ ,  $p + q=2$ ), provided by Air Products and Chemicals, Inc. of Allentown, PA, were prepared in the following manner. A volumetric flask was charged with varying amounts of surfactant. A certain amount of DI water was added to the volumetric flask to reach a level of 100 ml at room temperature. The mixture was agitated until the surfactant was dissolved therein to form the process solution. The amounts of surfactant in the process solutions of Examples 2a through 2d are provided in Table II.

**[0047]** Four 100 mm silicon wafers provided by Wafernet Inc. of San Jose, Ca. were coated with a SFR 510A phenolic resist coating provided by Shipley Inc. of Marlborough, Mass. using a spin coating process at a spin speed of 3200 rpm. The surfaces of resist-coated substrates were pre-wetted with Examples 2a through 2d process solutions. The resist-coated wafer was allowed to dry for a period of 20 seconds to remove excess water. Afterwards, the contact angles of 0.26N TMAH on the surface of the resist-coated substrates were measured. Table II lists the contact angle values at different drop ages expressed in seconds.

**[0048]** As Table II illustrates, the contact angles of TMAH developer on the resist-coated substrate that were treated with the process solutions of the present invention are smaller than the ones on the resist treated with DI water alone. This indicates that

surfactants are better adsorbed onto the resist-coated surface after treating with the process solutions of the present invention thereby improving the wetting between the developer and resist. Further, higher amounts of surfactant within the process solution may lead to more surfactant adsorption and more improved wetting.

5 TABLE II

Process Solution	Contact Angle (0 seconds)	Contact Angle (5 seconds)	Contact Angle (10 seconds)	Contact Angle (30 seconds)
Comp. Ex. 2 – DI water	46.7	40.8	38.1	31.4
Ex. 2a - 60 ppm surfactant	51.6	39.7	35.8	27.3
Ex. 2b -125ppm surfactant	52.1	37.2	33.3	25.0
Ex. 2c -250ppm surfactant	44.4	33.4	29.8	23.4
Ex. 2d -400 ppm surfactant	43.2	33.3	29.7	23.0

Examples 3a through 3c: Pre-Treatment of Substrate Surface with Process Solutions Containing Isopropyl Alcohol

**[0049]** Process solutions containing surfactant were prepared in the following manner.

10 A volumetric flask was charged with varying amounts of surfactant. A certain amount of isopropyl alcohol was added to the volumetric flask to reach a level of 100 ml at room temperature. The mixture was agitated until the surfactant was dissolved therein to form the process solution. The amounts and types of surfactant in the process solutions of Examples 3a through 3c are provided in Table III. Comparative Example 3 contains no  
15 surfactant - only isopropyl alcohol.

**[0050]** Wafers coated with SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> films were treated with hexamethyldisilazane (HMDS) vapor in an oven to improve the adhesion of the subsequent resist layer (e.g. polymethylglutarimide (PMGI) resist) for lift-off processing. After priming with the HMDS vapor, the surface became very hydrophobic, indicated by the contact angle of water

higher than 60°. As a result, the PMGI resist rolled off from the surface, making it difficult to obtain uniform film.

**[0051]** The surface hydrophobicity of the wafers were modified by contacting them with a process solution of comp. ex. 3 or examples 3a through 3c prior to coating the wafers with a resist coating. About 3mL of the process solution was dispensed on the wafer surface which was then spun at a speed of 500 rpm. After 5 seconds, the wafer was spun at 3000 rpm until dry. The contact angle of water was then measured on the wafer surface and the results were provided in Table III.

**[0052]** As Table III illustrates, the wafer surface becomes more hydrophilic after treatment with process solutions containing surfactant and isopropyl alcohol solutions because the contact angle is lowered. Consequently, the PMGI solution may no longer rolls off the surface and a uniform resist coating can be obtained more easily.

TABLE III

Process Solution	Surfactant	Contact angle (0 seconds)	Contact angle (5 seconds)	Contact angle (10 seconds)	Contact angle (30 seconds)
Comp Ex. 3 - No surfactant		63.5	63.3	63.2	62.5
Ex. 3a - 0.02wt%	m+n = 10, p+q = 0	58.2	58	58.2	57.8
Ex. 3b - 0.1wt%	m+n = 30, p+q = 0	46	50.4	50.9	51.5
Ex. 3c - 1.2wt%	m+n = 30, p+q = 0	29.9	42	43.1	43.5

**[0053]** While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.